^{1}H NMR Study of the Reaction of Iron(III) Porphyrins with NaBH$_4$ in the Presence of Alkenes. Formation of Organoiron(III) Porphyrins

Jun-ichiro SETSUNE,* Yoshihiro ISHIMARU, and Akira SERA

Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe 657

The treatment of [(tpp)Fe^{III}Cl] [tpp = tetraphenylporphyrin dianion] with NaBH$_4$ in the presence of alkenes afforded σ-type organoiron(III) porphyrins, the structure of which was analyzed by paramagnetic ^{1}H NMR. While 1-alkenes were hydrometallated to give σ-(1-methylalkyl)Fe^{III}(tpp) along with a small amount of σ-(alkyl)Fe^{III}(tpp), 2- and 3-alkenes yielded σ-(1-methylalkyl)Fe^{III}(tpp) complexes without any regioisomers.

It has been shown that hydridorhodium porphyrin undergoes insertion of alkenes and CO into a Rh^{III}-H bond via novel radical chain reactions with the quite reactive Rh^{II} porphyrin as a chain carrier.[1] Thus, unavailability of a vacant site cis to the hydrido ligand makes hydridometalloporphyrins quite different from ordinary metal hydrides in their properties and reactivities. The tendency of these hydridometalloporphyrins to liberate H$_2$ was noted[2] and this would be the reason why hydridocobalt and hydridoiron porphyrins have never been reported. We would like to describe here that iron porphyrin undergoes facile alkylation at iron with simple alkenes in the presence of a hydride donor such as NaBH$_4$. This suggests that alkenes are hydrometallated with a hydridoiron(III) porphyrin intermediate. As these organoiron(III) porphyrins are readily oxygenated to give ketones,[3] the present reaction would be closely related to the metalloporphyrin-catalyzed oxygenation[4] of alkenes with O$_2$ in the presence of NaBH$_4$ as a mimic for cytochrome P-450 system which utilizes NAD(P)H and O$_2$. That is, the catalytic oxygenation of alkenes to alcohols by Fe^{III}(tpp) and NaBH$_4$ is alternatively explainable in terms of organometallic chemistry of iron porphyrin, since ketone (or aldehyde) is readily converted into alcohol in the presence of a large excess amount of NaBH$_4$.

[(tpp)Fe^{III}Cl] (1) (0.07 mmol) was treated with 1-pentene (5 mmol) and NaBH$_4$ (5 mmol) in a mixture of toluene and methanol (4 mL : 0.1 mL) under argon at room temperature. The color of the solution changed from brown to red in a couple of minutes. The solvent was removed under vacuum and the residue was extracted with benzene. The benzene extract was purified by quickly passing through a short column of basic alumina under argon and then analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum in a degassed d$_6$ benzene solution showed signals due to σ-(pentyl)Fe^{III}(tpp) (4) and σ-(1-methylbutyl)Fe^{III}(tpp) (6) in a ratio of 1 : 4.4. Signals due to [Fe^{II}(tpp)] and [(Fe^{III}(tpp))$_2$O] were also observed as shown in Fig. 1.[3,5b] The total amount of these byproducts is similar to or less than that of σ-type organoiron(III) porphyrins. In the absence of alkenes, (1) was simply reduced to [Fe^{II}(tpp)]. Once (1) was reduced to [Fe^{II}(tpp)], further reaction did not occur even if alkenes were added afterwards. The reaction of 1-hexene instead of 1-pentene in the above procedure afforded a mixture of σ-(hexyl)Fe^{III}(tpp) (5) and σ-(1-methylpentyl)Fe^{III}(tpp) (7) in a ratio of 1 : 8.2 along with [Fe^{II}(tpp)] on the basis of the ^{1}H NMR. The structures of these σ-type organoiron(III) porphyrins were determined with referring
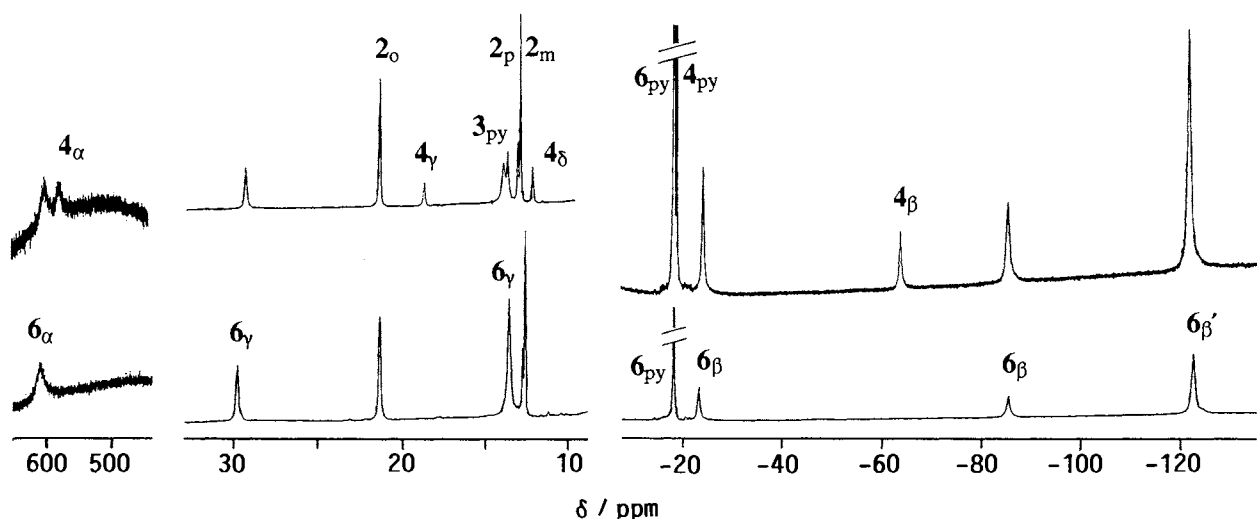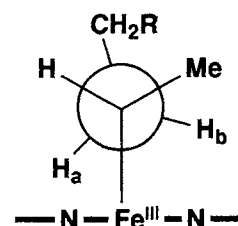
Fig. 1. ^{1}H NMR spectra (250 MHz, in C_6D_6 at 23 °C) of organoiron(III) complexes obtained from 1-pentene (top), and from 2-pentene (bottom). Signals due to [Fe^{II}(tpp)] and [(Fe^{III}(tpp))$_2$O] are labeled 2 and 3, those of σ-(pentyl)Fe^{III}(tpp) (4) and σ-(1-methylbutyl)Fe^{III}(tpp) (6) are labeled 4 and 6, respectively. Subscripts (α, β, γ, and δ) denote axial organo ligand protons relative to Fe. Subscripts (o, m, p, and py) denote porphyrin meso-phenyl (ortho, meta, para) and β-pyrrole protons.
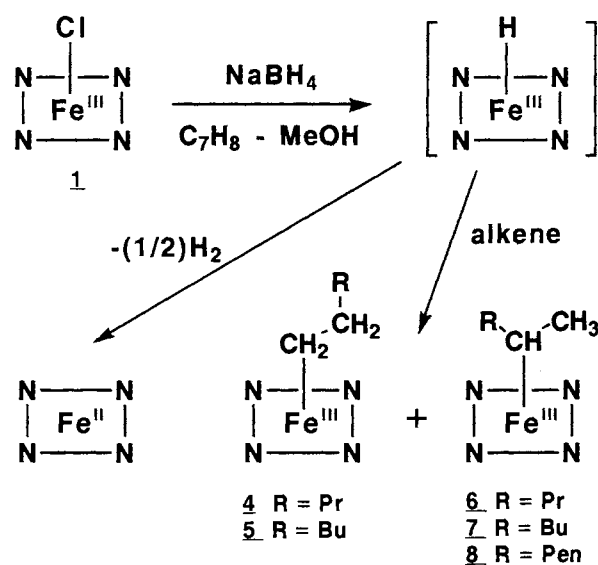
to the ^{1}H NMR chemical shifts of σ-(ethyl)Fe^{III}(tpp) (2)[6a] and σ-(butyl)Fe^{III}(tpp) (3)[6b] summarized in Table 1. Moreover, we have confirmed that the ^{1}H NMR spectrum of the organoiron(III) porphyrin prepared from (1) and 1-methylpentyl magnesium bromide is identical with that of (7). σ-(1-Methylalkyl)Fe^{III}(tpp) complexes showed a 3H-signal at a region (ca. -120 ppm) characteristic of a β-methyl group with respect to Fe. Furthermore, the chiral center at the α-carbon makes the β-pyrrole, and β-, γ-, and δ-CH$_2$ signals split into two groups. The chemical shift difference between two β-CH$_2$ protons is particularly large (ca. 60 ppm). The isotropic shifts for these β-CH$_2$ protons mainly of a contact origin are dependent on the dihedral angle [∠(Fe-C-C-H)] just like a vicinal coupling constant in diamagnetic ^{1}H NMR.[5] Therefore, the resonances at around -80 ppm are associated to H$_a$ and those at around -20 ppm are associated to H$_b$, because the dihedral angle [∠(Fe-C-C-H$_a$)] is less than 60 degree while that [∠(Fe-C-C-H$_b$)] is more than 60 degree due to the steric repulsion between the β'-CH$_3$ and the γ-CH$_2$R group. Of particular interest is the observation of α-CH or α-CH$_2$ signals at around 600 ppm as shown in Fig. 1. The alteration of the sign of isotropic shifts upon going from α-CH to γ-CH signal is indicative of the spin polarization mechanism for the transmission of the spin on the iron to the axial organo ligand.[5a]

We have recently demonstrated that σ-type organocobalt(III) porphyrins are formed in good yields, when an oxidizing agent (t-BuOOH or O$_2$) is added to a mixture of Co^{II} porphyrin, alkene, and NaBH$_4$.[7] Hydridocobalt(III) and hydridoiron(III) porphyrin would be responsible for the hydrometallation of alkenes in competition with bimolecular H$_2$ evolution to generate metal(II) porphyrin as shown in Scheme 1. While reoxidation of Co^{II} to Co^{III} in situ led to excellent yields of organocobalt(III) porphyrins because a hydridocobalt(III) intermediate would be regenerated in the presence of excess NaBH$_4$, it was difficult to reoxidize Fe^{II} to Fe^{III} without destroying organoiron(III) porphyrins due to their extremely air-sensitive nature.

While 1-pentene and 1-hexene gave a mixture of regioisomeric organoiron(III) complexes as noted above,

2-pentene and 2-hexene yielded σ-(1-methyl-alkyl)Fe^{III}(tpp), (6 and 7), without regioisomers in a detectable amount under the same reaction conditions. Furthermore, σ-(1-methylhexyl)-Fe^{III}(tpp) (8) was found to be the sole organoiron(III) porphyrin product when 3-heptene was allowed to react in a similar manner. These facts indicate that the regioselectivity in the hydrometallation of alkenes with iron porphyrin is basically determined by the stability of the organic radicals (tertiary > secondary > primary) generated through the addition of a hydrogen radical to alkenes. However, a tertiary alkyl radical or a congested secondary alkyl radical can not make a stable Fe^{III}-C bond due to the steric repulsion with a porphyrin ligand.$^{5b)}$ Thus, σ-(1-ethylalkyl)Fe^{III}(tpp) complexes which should take place in the reaction of 2- and 3-alkenes could not be observed but rearranged via β-elimination - addition sequence of a Fe^{III}-H bond with a C-C double bond to give σ-(1-methylalkyl)Fe^{III}(tpp) complexes (6 - 8).

Scheme 1.

Table 1. ^{1}H NMR data of σ-type organoiron(III) porphyrin complexes in C_6D_6 at 23 °C

Complexes	Chemical shifts (δ-value from TMS)$^{a)}$							
	Porphyrin β-pyrrole		Axial organo ligand					
		β'-	α-	β-	γ-	δ-	ε-	ζ-
(2)$^{b)}$	-18.9(8H)	-117(3H)	-d)	-	-	-	-	-
(3)$^{c)}$	-18.4(8H)	-	-d)	-63.7(2H)	18.2(2H)	10.3(3H)	-	-
(4)	-18.5(8H)	-	580(2H)	-63.5(2H)	18.4(2H)	11.9(2H)	n.d.	
(5)	-18.4(8H)	-	580(2H)	-60.8(2H)	18.7(2H)	12.2(2H)	n.d.	n.d.
(6)	-17.81(4H) -17.90(4H)	-122(3H)	600(1H)	-23.7(1H) -85.2(1H)	29.2(1H) 13.6(1H)	7.9(3H)	-	-
(7)	-17.50(4H) -17.54(4H)	-120(3H)	600(1H)	-25.6(1H) -81.1(1H)	28.7(1H) 14.2(1H)	9.4(1H) 8.7(1H)	3.6(3H)	-
(8)	-17.50(4H) -17.56(4H)	-120(3H)	600(1H)	-22.6(1H) -79.1(1H)	29.1(1H) 13.6(1H)	9.9(1H) 9.0(1H)	5.1(1H) 4.9(1H)	3.2(3H)

a) β'-, α-, β-, γ-, δ-, ε-, ζ- are positions relative to the metal center. Signal multiplicity is singlet. b) Taken from Ref. 4a. c) Taken from Ref. 4b. d) Not reported.

In conclusion, hydrometallation of alkenes with [(tpp)Fe^{III}Cl] and NaBH$_4$ occurred to give σ-(1-methyl-alkyl)Fe^{III}(tpp) complexes. Work is now going on to further study the role of organoiron(III) porphyrin complexes in catalytic oxygenation reactions.

References

1) B. B. Wayland and B. A. Woods, *J. Chem. Soc., Chem. Commun.*, **1981**, 700; B. B. Wayland, B. A. Woods, and V. M. Minda, *ibid.*, **1982**, 634; R. S. Paonessa, N. C. Thomas, and J. Halpern, *J. Am. Chem. Soc.*, **107**, 4333 (1985).

2) J.-i. Setsune, Z.-I. Yoshida, and H. Ogoshi, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 983; J. P. Collman, J. E. Hutchison, P. S. Wagenknecht, N. S. Lewis, M. A. Lopez, R. Guilard, *J. Am. Chem. Soc.*, **112**, 8206 (1990).

3) R. D. Arasasingham, A. L. Balch, C. R. Cornman, and L. Latos-Grazynski, *J. Am. Chem. Soc.*, **111**, 4357 (1989).

4) T. Santa, T. Mori, and M. Hirobe, *Chem. Pharm. Bull.*, **33**, 2175 (1985); T. Mori, T. Santa, and M. Hirobe, *Tetrahedron Lett.*, **26**, 5555 (1985); I. Tabushi and N. Koga, *J. Am. Chem. Soc.*, **101**, 6456 (1979); M. Perree-Fauvet and A. Gaudemer, *J. Chem. Soc., Chem. Commun.*, **1981**, 874; Y. Ohkatsu, M. Ohno, T. Ooi, and S. Inoue, *Nippon Kagaku Kaishi*, **1985**, 387; T. Okamoto and S. Oka, *J. Org. Chem.*, **49**, 1589 (1984); K. Kano, H. Takagi, M. Takeuchi, S. Hashimoto, and Z.-I. Yoshida, *Chem. Lett.*, **1991**, 519.

5) a) G. N. La Mar, "NMR of Paramagnetic Molecules," ed by G. N. La Mar, W. D. Horrocks Jr., R. H. Holm, Academic Press, New York (1973), pp.85-126; b) A. L. Balch, R. L. Hart, L. Latos-Grazynski, and T. G. Traylor, *J. Am. Chem. Soc.*, **112**, 7382 (1990).

6) a) A. L. Balch, C. R. Cornman, and N. Safari, *Organometallics*, **9**, 2420 (1990); b) P. Cocolios, G. Lagrange, and R. Guilard, *J. Organomet. Chem.*, **253**, 65 (1983).

7) J.-i. Setsune, Y. Ishimaru, T. Moriyama, and T. Kitao, *J. Chem. Soc., Chem. Commun.*, **1991**, 555.